

## PATENT COOPERATION TREATY

PCT

REC'D 19 APR 2006

WIPO

PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference Cal 88777	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416)	
International application No. PCT/EP2004/012746	International filing date (day/month/year) 09.11.2004	Priority date (day/month/year) 14.11.2003
International Patent Classification (IPC) or both national classification and IPC INV. C08F4/651 C08F4/654 C08F10/02		
Applicant POLIMERI EUROPA S.P.A. et al.		



1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 7 sheets, including this cover sheet.
 

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 9 sheets.

3. This report contains indications relating to the following items:

- |      |                                     |  |
|------|-------------------------------------|--|
| I    | <input checked="" type="checkbox"/> | Basis of the opinion   |
| II   | <input type="checkbox"/>            | Priority   |
| III  | <input type="checkbox"/>            | Non-establishment of opinion with regard to novelty, inventive step and industrial applicability   |
| IV   | <input type="checkbox"/>            | Lack of unity of invention   |
| V    | <input checked="" type="checkbox"/> | Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement |
| VI   | <input type="checkbox"/>            | Certain documents cited  |
| VII  | <input type="checkbox"/>            | Certain defects in the international application   |
| VIII | <input checked="" type="checkbox"/> | Certain observations on the international application  |

Date of submission of the demand  09.06.2005	Date of completion of this report  20.04.2006
Name and mailing address of the international preliminary examining authority:   European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer  Parry, J  Telephone No. +31 70 340-1032 

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. **PCT/EP2004/012746**

**I. Basis of the report**

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*):

**Description, Pages**

1-15, 17-48 as originally filed  
16 received on 15.09.2005 with letter of 13.09.2005

**Claims, Numbers**

1-53 as originally filed

**Claims, Pages**

49, 53, 54, 56-60 received on 15.09.2005 with letter of 13.09.2005

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).  
☐ the language of publication of the international application (under Rule 48.3(b)).  
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.  
☐ filed together with the international application in computer readable form.  
☐ furnished subsequently to this Authority in written form.  
☐ furnished subsequently to this Authority in computer readable form.  
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.  
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:  
☒ the claims, Nos.: 53  
☐ the drawings, sheets:

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. **PCT/EP2004/012746**

5. ☒ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

**see separate sheet**

6. Additional observations, if necessary:

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes: Claims	2-6,12,14-31,41-52
	No: Claims	1,7-11,13,32-40
Inventive step (IS)	Yes: Claims	
	No: Claims	1-52
Industrial applicability (IA)	Yes: Claims	1-52
	No: Claims	

2. Citations and explanations

**see separate sheet**

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

**see separate sheet**

**Re Item I**

**Basis of the opinion**

1. The amendment of claims 2 and 15 omitting "suitable" violates Art. 34 PCT, as now any granular solid is intended, and not just those which are suitable in the present context.
2. The "size" of original claims 4 and 16, and p.16 can be construed by the skilled person as referring to the sole dimension possessing the greatest value, as expressed also by the Applicant in point 2 of the reply of 13.09.05, and is therefore not equal in meaning to the term "dimensions", which is plural. The amendment thus violates Art. 34 PCT.
3. Claim 14: original claim 30 does not depend on original claim 14, so the basis for the amendment to claim 14 cannot be readily seen.
4. It should have been specified in justifying support for amendments whether reference was being made to the original claims or amended claims, also all changes over the claims as originally filed should have been indicated on a marked-up copy.

**Re Item V**

**Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability: citations and explanations supporting such statement**

The following documents (D1-D5) will be referred to (see the ISR for the relevant passages):

- D1: US-B1-6 200 923 (GAROFF THOMAS ET AL) 13 March 2001 (2001-03-13)
- D2: US-A-5 780 378 (SHINOZAKI TETSUNORI ET AL) 14 July 1998 (1998-07-14)
- D3: EP-A-0 768 322 (SUMITOMO CHEMICAL CO) 16 April 1997 (1997-04-16)
- D4: US-A-5 324 805 (NISHIKAWA HIROSHI ET AL) 28 June 1994 (1994-06-28)
- D5: US-A-5 290 745 (JORGENSEN ET AL) 1 March 1994 (1994-03-01)

1. D1 describes a catalytic composition comprising  $\text{MgCl}_2 \cdot 3\text{EtOH}$  (Dp),  $\text{TiCl}_4$  and di-undecylphthalate internal electron donor (D) which possesses the following molar ratios of reagents:  $\text{Mg/Ti}=1,55$   $\text{EtOH/D}=0,31$   $\text{D/Ti}=0,966$ . The  $\text{Cl/Ti}$  and cocatalyst metal (Al):Ti and Al:(D+Dp) ratios are not disclosed but are likely to fall under those mentioned in present claims 1, 32, and 37 respectively. Eg 3 describes the precipitation of a clearly solid composition, and table 3 is specifically headed: "chemical composition of the solidified composition" and so also concerns solid compositions where in the fourth column the number of mol of Mr per mol Ti as being 1.55. The amount of ethoxide being formed is

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP2004/012746

small in lines 43-47 of col. 7, so that the majority exists as EtOH as clearly mentioned in the third line of table 3, ie "EtO-" in the form of "EtOH". It is thus clearly EtOH which is being described as being present here and not ethoxide. The present process according to original claim 14 occurs in solution, not in the solid state. Hence present claims 1,7-11,13,32-40 are not novel and it is not necessary to consider the inventivity of these claims.

2. Starting from the teachings of D1, over which there are no comparative examples, it is trivial to use a granular support such as silica. Such supports are standard in the art (see D5). Hence present claims 2-6 are not inventive.

3. Starting from the teachings of D1, it is likewise trivial to vary D for other similar compounds which are standard in the art (see D2-D4). Hence present claim 12 is not inventive.

4. Starting from the combined teachings of D1 and D5, and in the absence of any demonstrated technical effect, it is trivial to vary the process steps for the preparation of these catalysts by employing other techniques which are standard in the art. Hence present claims 14-31 are not inventive.

5. It is trivial to use the catalysts of D1 for (gas phase) ethylene (co)polymerisation instead of propylene polymerisation. Hence present claims 41-52 are not inventive.

**Re Item VIII**

**Certain observations on the international application**

The following objections are made under Art. 6 (PCT):

1. Claims 2 and 15: the term "suitable granular form" is unclear. Anyway, the amendment has been ignored ( see Box I). "Inert" is unclear as it has not been defined with respect to a point of reference within the context of the present application. Likewise claims 15, 27,28.

2. Claims 4 and 16: which "dimension" is being referred to? The amendment has been ignored ( see Box I).

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

---

International application No. PCT/EP2004/012746

3. Claim 5: "porosity" and "radius" as measured by what technique? Several methods exist for measuring these parameters from which the skilled person can choose, and not just the BET method for the former. For example there are even several techniques that fall under the BET method and there is also the mercury intrusion method for measuring porosity.
4. Claim 9: an aromatic alcohol cannot have "2" carbon atoms. It would have been better if it had been made clear which value for the index for C referred to aromatic compounds.
5. Original claim 14: the expression: "..until the desired solid..." describes a "result to be achieved" (PCT GL Ch.-III,4.7). The amendment has been ignored ( see Box I).
6. Claim 22: the term "..until at least.." describes a "result to be achieved" (PCT GL Ch.-III,4.7) irrespective of whether the skilled person can verify this or not, because the nature of the mixture may be such that it is impossible to dissolve 80% of the Ti and Mg compounds.
7. Original claims 32,34-41: these are product claims. It cannot necessarily be ascertained that an organoaluminium had been added if the alkyl groups thereon became protonated off by Dp.
8. Original claims 37-41 are product claims. It cannot necessarily be ascertained in the product that activation occurred with another Al reagent. The Al reagents cannot in any case be distinguished from one another.
9. Original claims 42-53: these are process claims making use of catalyst products themselves produced by processes. It cannot necessarily be ascertained that the catalyst product was indeed produced beforehand in this way.
10. Original claim 50: "sufficient" is unclear.
11. Original claim 44 ("partially comprising a stream in liquid form") cannot depend on claim 43, as the latter only refers to gas phase polymerisation and a gaseous stream. If the intention was to refer to an inlet carrying liquid material before the reactor, then this should have been made clear.

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

---

International application No. PCT/EP2004/012746

12. Original claims 47-53 describe processes for producing various desired types of polyethylene and as such define "results to be achieved" (PCT GL Ch.-III,4.7) Whatever the skilled person knows about manipulating said parameters in a general sense may not be applicable to this specific process. For example, it may be impossible to arrive at such a low value of Mw/Mn of 2.5 (original claim 53) for a Ziegler-Natta catalyst, or to produce linear polyethylene of said density or ensure the specified Mw range is attained, alone or in combination with the other parameters.

tively available, or it can act as a thickening agent in the subsequent step (b) for the preparation of the catalytic solid. Inert solids suitable for the purpose are certain polymers in granule or powder form such as polystyrene  
5 or polyester, possibly modified according to the known art. Inorganic solids such as natural or synthetic silica are preferably used, in its various varieties, also commercially available, titania, silico-aluminates, calcium carbonate, magnesium chloride (in a substantially insoluble  
10 form), or a combination thereof. Said inert solids I are preferably in granular form with average granule size ~~dimensions~~ ranging from 10  $\mu\text{m}$  to 300  $\mu\text{m}$ , and a narrow size distribution. A silica typically suitable for the purpose is a microspheroidal silica (size 20-100  $\mu\text{m}$ ) having a BET  
15 surface area ranging from 150 to 400  $\text{m}^2/\text{g}$ , a total porosity equal or higher than 80% and an average pore radius of 50 to 200  $\text{\AA}$ .

The quantity of inert solid added to the mixture in (a) is generally selected by normal experts on the basis of  
20 the role of the inert solid in the catalyst or in its preparation. Such quantities are conveniently used as to obtain at the end of the preparation a content of inert product ranging from 10 to 90%, preferably from 20 to 70%, by weight with respect to the total weight of the solid  
25 component. In particular, if the inert solid is mainly in-



CLAIMS

1. A solid component of catalyst for the (co)polymerization of ethylene, comprising titanium, magnesium, chlorine, an organo-oxygenated protic compound  $D_p$ , and a neutral electron-donor aprotic compound D, in the following molar ratio ranges:  
 $Mg/Ti = 1.0-50$ ;  $D/Ti = 1.0-15$ ;  
 $Cl/Ti = 6.0-100$ ;  $D_p/D = 0.05-3$ .
2. The solid component according to claim 1, additionally comprising an inert granular solid ~~an inert solid I in a suitable granular form~~, in a quantity ranging from 10 to 90% by weight with respect to the total weight of the solid component.
3. The solid component according to claim 2, wherein said inert solid I is in a quantity ranging from 25 to 50% by weight.
4. The solid component according to any of the previous claims, wherein said inert solid I is selected from granular inorganic solids included in the group: silica, titania, silico-aluminates, calcium carbonate, magnesium chloride, having average sizes ~~dimensions~~ of the granule ranging from 10  $\mu m$  to 300  $\mu m$ .
5. The solid component according to claim 4, wherein said solid I consists of microspheroidal silica having an average diameter ranging from 20 to 100  $\mu m$ , a BET sur-

taining the mixture for a period varying from 5 minutes to 5 hours. ~~until the desired solid component of catalyst is formed.~~

15. The process according to claim 14, wherein, in step

5 (a) an inert granular solid ~~an inert solid I in a suitable granular form,~~ is also added.

16. The process according to the previous claim 15, wherein said inert solid I is selected from granular inorganic solids included in the group: silica, titania, silico-aluminates, calcium carbonate, magnesium  
10 chloride, having average granule sizes ~~dimensions~~ ranging from 10  $\mu\text{m}$  to 300  $\mu\text{m}$ .

17. The process according to the previous claims 15 or 16, wherein said inert solid I consists of microspheroidal  
15 silica having an average diameter ranging from 20 to 100  $\mu\text{m}$ , a BET surface area ranging from 150 to 400  $\text{m}^2/\text{g}$ , a total porosity equal or higher than 80% and an average pore radius of 50 to 200 Å.

18. The process according to any of the previous claims  
20 from 14 to 17, wherein said titanium compound having formula (I) ~~is essentially soluble in said compound D~~ and is selected from titanium chlorides, bromides, alcoholates and carboxylates.

19. The process according to any of the previous claims  
25 from 14 to 17, wherein said compound having formula

(I) in step (a) is titanium trichloride.

20. The process according to any of the previous claims from 14 to 19, wherein said magnesium chloride is in amorphous ~~or semi-amorphous~~ form.

5 21. The process according to any of the previous claims from 14 to 20, wherein, in said step (a), the atomic ratio between magnesium and titanium ranges from 1.0 to 50 and the ratio (D moles)/(Ti atoms) ranges from 5 to 100.

10 22. The process according to any of the previous claims from 14 to 21, wherein said step (a) is carried out at a temperature ranging from room temperature to the boiling point of the donor compound D, ~~for a time varying from a few minutes to 24 hours~~, until at least  
15 80% of said compounds of Ti and Mg have been dissolved.

23. The process according to any of the previous claims from 14 to 22, wherein said step (b) is carried out by means of evaporation, preferably by spray-drying.

20 24. The process according to any of the previous claims from 14 to 23, wherein the molar ratio  $D_p/D$  in said step (d) ranges from 0.2 to 1.2.

25 25. The process according to any of the previous claims from 14 to 24, wherein said step (d) is carried out by heating the mixture to a temperature ranging from 40

29. The process according to any of the previous claims 27 and 28, wherein the molar ratio  $D_p/D$  in said step ranges from 0.2 to 1.2.

30. The process according to any of the previous claims  
5 from 27 to 29, wherein said reaction is carried out at a temperature ranging from 40 to 100°C, for a period varying from 5 minutes to 5 hours.

31. The process according to the previous claim 30,  
10 wherein said reaction is carried out at a temperature ranging from 60 to 80°C, for a period of 5 to 60 minutes.

32. A catalyst for the (co)polymerization of ethylene,  
which is obtained by means of contact and reaction of  
said solid component according to any of the previous  
15 claims from 1 to 13, with a co-catalyst comprising a hydrocarbyl compound of a metal selected from Al, Ga, Mg, Zn and Li, wherein the atomic ratio between the metal in the co-catalyst and titanium in the solid component of catalyst ranges from 10:1 to 500:1.

20 33. The catalyst according to claim 32, wherein the atomic ratio between the metal in the co-catalyst and titanium in the solid component of catalyst ranges from ~~10:1 to 500:1~~ and preferably from 50:1 to 200:1.

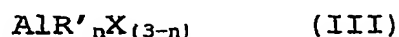
34. The catalyst according to claim 32 or 33, comprising  
25 titanium, magnesium, aluminum and chlorine, wherein

said co-catalyst comprises an alkylic organometallic compound of aluminum.

35. The catalyst according to claim 34, wherein said organometallic compound of aluminum is selected from aluminum tri-alkyls containing from 1 to 10 carbon atoms in each alkyl group.

~~36. The catalyst according to any of the claims from 32 to 35, wherein the contact between the solid component and co-catalyst is obtained in situ in the polymerization reactor.~~

36  
37. The catalyst according to any of the claims from 32 to 356, wherein said solid component is activated before contact with said co-catalyst, by reaction with an aluminum alkyl or alkyl chloride represented by the following general formula (III):



wherein: R' is a linear or branched alkyl radical containing from 1 to 20 carbon atoms, X is selected from H and Cl, preferably Cl, and "n" is a decimal number having values ranging from 1 to 3, preferably from 2 to 3;

in such a quantity that the Al/(D+D<sub>p</sub>) ratio between the aluminium moles in said compound having formula (III) and the total of D and D<sub>p</sub> moles in said solid component, ranges from 0.1 to 1.5.

- 37  
38. The catalyst according to claim <sup>36</sup>37, wherein said R' in formula (III) is a linear or branched aliphatic radical, having from 2 to 8 carbon atoms.
- 38  
39. The catalyst according to anyone of the previous claims <sup>36</sup>37 and <sup>37</sup>38, wherein said Al/(D+D<sub>p</sub>) ratio ranges from 0.2 to 1.3, preferably from 0.3 to 1.0.
- 40  
40. The catalyst according to any of the previous claims from <sup>36</sup>37 to <sup>38</sup>39, wherein said solid component is activated in two successive steps by reaction in the first step with an aluminum trialkyl (n = 3 in formula (III)), and in the second step with an aluminum dialkyl chloride (n = 2, X = Cl, in formula (III)), in such a quantity that the overall molar ratio Al/(D+D<sub>p</sub>) ranges from 0.1 to 1.3, preferably from 0.4 to 1.1.
- 41  
41. The catalyst according to claim <sup>38</sup>40, wherein, in said first step the molar ratio AlR<sub>3</sub>/(D+D<sub>p</sub>) ranges from 0.1 to 0.4 and in the second step the molar ratio AlR<sub>2</sub>Cl/(D+D<sub>p</sub>) ranges from 0.2 to 0.6.
- 41  
42. A process for the (co)polymerization of ethylene, comprising reacting ethylene and optionally at least one alpha-olefin, under suitable polymerization conditions, in the presence of said catalyst according to any of the previous claims from 32 to <sup>40</sup>41.
- 42  
43. The process according to claim <sup>41</sup>42, carried out in gas phase with the fluid-bed method, wherein a gaseous

stream of ethylene and optional alpha-olefin is reacted in the presence of a sufficient quantity of catalyst, wherein the titanium concentration ranges from 1 to 5 ppm by weight with respect to the consolidated production, at a temperature ranging from 70 to 115°C, and at a pressure ranging from 500 to 1000 kPa.

<sup>43</sup>  
~~44~~. The process according to the previous claim <sup>42</sup>~~43~~, wherein said stream is introduced from the bottom of the polymerization reactor, partially comprising a stream in liquid form.

<sup>44</sup>  
~~45~~. The process according to anyone of claim <sup>42</sup>~~43~~ and <sup>43</sup>~~44~~, in the presence of a catalyst according to any of the previous claims from 37 to 41.

<sup>45</sup>  
~~46~~. The process according to any of the preceeding claims from <sup>41</sup>~~42~~ to <sup>44</sup>~~45~~, wherein the molar ratio with ethylene ranges from 0.1 to 1.0.

<sup>46</sup>  
~~47~~. The process according to any of the preceeding claims from <sup>41</sup>~~42~~ to <sup>45</sup>~~46~~, wherein said  $\alpha$ -olefin is selected from 1-butene, 1-hexene and 1-octene and is in such a quantity that the molar ratio with ethylene ranges from 0.1 to 0.4.

<sup>47</sup>  
~~48~~. The process according to any of the preceeding claims from <sup>41</sup>~~42~~ to <sup>46</sup>~~47~~, for obtaining linear polyethylene having a density ranging from 0.915 to 0.950 g/ml,

<sup>48</sup>  
~~49~~. The process according to any of the preceeding claims

from <sup>42</sup>~~43~~ to <sup>46</sup>~~47~~ for obtaining linear polyethylene having a density lower than 0.915 g/ml, preferably ranging from 0.900 to less than 0.915 g/ml, comprising the copolymerization in gas phase of a gaseous mixture including ethylene and at least one alpha-olefin having from 4 to 10 carbon atoms.

<sup>48</sup>~~50~~. The process according to claim <sup>48</sup>~~49~~, wherein the gaseous mixture of ethylene and the at least one alpha-olefin is reacted in the presence of a sufficient quantity of catalyst, at a temperature ranging from 70 to 95°C, and a pressure ranging from 500 to 1000 kPa.

<sup>50</sup>~~51~~. The process according to any of the previous claims <sup>48</sup>~~49~~ and <sup>48</sup>~~50~~, wherein said alpha-olefin is selected from 1-butene, 1-hexene and 1-octene, and is in such a quantity that the molar ratio with respect to ethylene ranges from 0.1 to 0.4.

<sup>51</sup>~~52~~. The process according to any of the previous claims from <sup>41</sup>~~42~~ to <sup>50</sup>~~51~~, wherein said catalyst is formed *in situ* inside the reactor.

<sup>52</sup>~~53~~. The process according to any of the previous claims from <sup>41</sup>~~42~~ to <sup>51</sup>~~52~~, wherein said linear polyethylene has a weight average molecular weight  $M_w$  ranging from 20,000 to 500,000 and a MWD ( $M_w/M_n$ ) distribution ranging from 2.5 to 4.